PB86-201241

Variability of Aquifer Sorption Properties in a Field Experiment on Groundwater Transport of Organic Solutes: Methods and Preliminary Results

Stanford Univ., CA

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

1986

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	PB86-201241
EPA/600/J-86/055		

4. TITLE AND SUBTITLE
VARIABILITY OF AQUIFER SORPTION PROPERTIES IN A FIELD EXPERIMENT ON GROUNDWATER TRANSPORT OF ORGANIC SOLUTES: Methods and Preliminary Results

5. REPORT DATE
1986

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
(Journal Version)
D.M. Mackay, W.P. Ball, and M.G. Durant

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Civil Engineering
Stanford University
Stanford, California 94305

10. PROGRAM ELEMENT NO.
CBWD1A

11. CONTRACT/GRANT NO.
CR-808851

12. SPONSORING AGENCY NAME AND ADDRESS
Robert S. Kerr Environmental Research Lab. - Ada, OK
Office of Research and Development
U.S. Environmental Protection Agency
Ada, OK 74820

13. TYPE OF REPORT AND PERIOD COVERED
Interim

14. SPONSORING AGENCY CODE
EPA/600/15

15. SUPPLEMENTARY NOTES
Published in JOURNAL OF CONTAMINANT HYDROLOGY, 1(1986):119-132
Elsevier Science Publishers B.V., Amsterdam--Printed in The Netherlands

16. ABSTRACT

Methods to characterize the organic solute sorption distribution coefficient, organic carbon content, and specific surface area of aquifer solids from the site of a field experiment on solute transport in groundwater were refined for application to small subsamples of 10-cm depth increments taken from 5-cm diameter cores. Initial results indicate that the average sorption characteristics of the Borden aquifer do not vary appreciably along the trajectory of the solute plumes. However, the sorption distribution coefficient of tetrachloroethylene varied over nearly an order of magnitude among 10-cm depth increments in one core sample. Preliminary evidence suggests that the sorption distribution coefficients for four halogenated organic solutes vary proportionally among core strata. However, the distribution coefficients for sorption of tetrachloroethylene on various depth increments are not well correlated with either organic carbon content or specific surface area, suggesting that as yet unidentified mineral phases may play a significant role in sorption of such solutes by the sandy aquifer solids.

→ P 119

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO THE PUBLIC.	UNCLASSIFIED	15
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77)

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA/600/J-86/055
JOURNAL ARTICLE

Journal of Contaminant Hydrology, 1 (1986) 119—132
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

VARIABILITY OF AQUIFER SORPTION PROPERTIES IN A FIELD EXPERIMENT ON GROUNDWATER TRANSPORT OF ORGANIC SOLUTES: METHODS AND PRELIMINARY RESULTS

D.M. MACKAY, W.P. BALL and M.G. DURANT
Department of Civil Engineering, Stanford University, Stanford, CA 94305 (U.S.A.)

(Received December 20, 1984; revised and accepted September 18, 1985)

ABSTRACT

Mackay, D.M., Ball, W.P. and Durant, M.G., 1986. Variability of aquifer sorption properties in a field experiment on groundwater transport of organic solutes: Methods and preliminary results. In: D.L. Macalady (Editor), Transport and Transformations of Organic Contaminants. J. Contam. Hydrol., 1: 119—132.

Methods to characterize the organic solute sorption distribution coefficient, organic carbon content, and specific surface area of aquifer solids from the site of a field experiment on solute transport in groundwater were refined for application to small subsamples of 10-cm depth increments taken from 5-cm diameter cores. Initial results indicate that the average sorption characteristics of the Borden aquifer do not vary appreciably along the trajectory of the solute plumes. However, the sorption distribution coefficient of tetrachloroethylene varied over nearly an order of magnitude among 10-cm depth increments in one core sample. Preliminary evidence suggests that the sorption distribution coefficients for four halogenated organic solutes vary proportionally among core strata. However, the distribution coefficients for sorption of tetrachloroethylene on various depth increments are not well correlated with either organic carbon content or specific surface area, suggesting that as yet unidentified mineral phases may play a significant role in sorption of such solutes by the sandy aquifer solids.

INTRODUCTION

A field experiment on solute transport in groundwater has been conducted at a site in Borden, Ontario, by a group of investigators at Stanford University and The University of Waterloo (Mackay et al., 1985). Since August 1982, natural gradient transport of a large injected pulse of two conservative tracers and five halogenated organic solutes has been monitored in detail in three dimensions using a network of multilevel sampling devices. Examination of the data has indicated that there was considerable variability in solute concentration as a function of depth in profiles through the migrating solute pulses (Mackay et al., 1985). In addition, for a given plan position, solute breakthrough times varied with depth. Lastly, there is some evidence that, for certain of the organic solute pulses, both the mass in solution and the velocity of the center of mass of the pulse decreased over the two-year monitoring period (Roberts et al., 1985).

0169-7722/86/$03.50 © 1986 Elsevier Science Publishers B.V.

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

Such phenomena could be due to the combined effects of mass transport limitations, solute transformation and spatially variable hydraulic conductivity and sorption characteristics. The first two of these have been discussed elsewhere (Criddle et al., this volume; Goltz and Roberts, this volume). This paper summarizes the initial results of the analysis of sorption characteristics of core samples from the field site.

DESCRIPTION OF THE FIELD EXPERIMENT AND SITE

The experiment is being conducted in an unconfined sand aquifer which extends vertically from a nearly horizontal quarry floor to a thick silty clay deposit at a depth of about 9 m. The aquifer material is a clean, well-sorted, fine- to medium-grained sand of glaciofluvial origin. Although the aquifer is quite homogeneous relative to many aquifers of glaciofluvial or fluvial origin, undisturbed cores reveal distinct bedding features. The bedding is primarily horizontal and parallel, although some cross-bedding and convolute bedding are observed. The texture of individual strata ranges from silt to coarse sand with occasional pebbles. Additional detail on aquifer characteristics as well as groundwater chemistry and hydrology at the site is provided elsewhere (Dance, 1980; O'Hannesin, 1981; MacFarlane et al., 1983; Mackay et al., 1985).

Detailed characterization of the spatial variability of hydraulic conductivity at the site is being undertaken by the University of Waterloo, Department of Earth Sciences. Analysis of the data from 5-cm subsections of 32 cores suggests that the horizontal correlation length scale is on the order of 1.5 m while the vertical correlation length scale is approximately 0.1 m (Sudicky, 1985). The grain-size data of O'Hannesin (1981) also suggest vertical correlation scales on the order of 0.05—0.10 m.

Figure 1 shows a plan view of the field site. Multilevel sampling devices (Cherry et al., 1983) were installed at horizontal intervals of 1.0—4.0 m with vertical intervals between sampling points of 0.2—0.3 m. In August 1982, using equipment and procedures described elsewhere (Mackay et al., 1985), 12 m^3 of a uniform solution was injected as a pulse into the saturated zone through the nine injection wells shown in Fig. 1. The injection solution was local groundwater spiked with the solutes listed in Table 1 to yield injection concentrations also listed therein. Monitoring of the migrating solute pulses is described elsewhere (Mackay et al., 1985; Roberts et al., 1985). Figure 1 also depicts the locations at which bulk and core samples of the aquifer material were taken by the Department of Earth Sciences, University of Waterloo. The 360-kg bulk sample was excavated with a 16.5-cm auger from the depth interval 1—4 m. Core samples were acquired by driving 5-cm inside-diameter (ID) aluminum tubes into the deposit and jacking them out using precautions to prevent disturbance or loss of the tube contents.

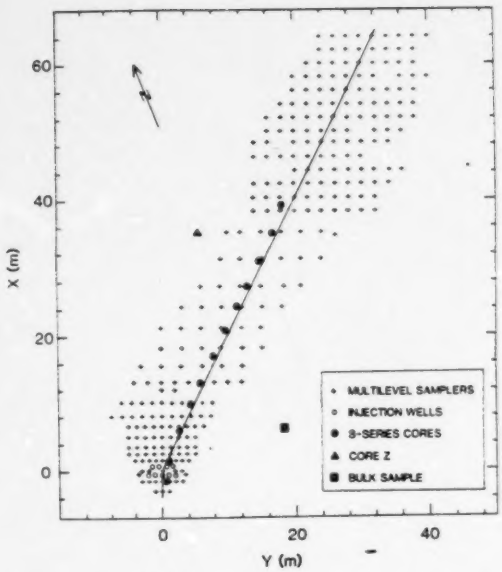

Fig. 1. Experimental site and instrumentation. The plan view shows multilevel samplers and injection wells and the locations at which core and bulk samples of the aquifer solids were taken. The solid line indicates the trajectory of the centers of mass of the migrating solutes. S-series cores are numbered consecutively from 1 to 12 beginning near the origin.

TABLE 1

Composition of injection solution and sorption distribution coefficients (K_d) measured with the bulk sample of aquifer material

Solute	Injection concentration	K_d ($m^3\ g^{-1}$)	
		isotherm[a]	one-point[b]
chloride	892 $mg\ l^{-1}$	—	—
bromide	324 $mg\ l^{-1}$	—	—
carbon tetrachloride	31 $\mu g\ l^{-1}$	1.65 ± 0.15	1.3 ± 0.1
bromoform	32 $\mu g\ l^{-1}$	1.73 ± 0.20	—
tetrachloroethylene	30 $\mu g\ l^{-1}$	4.60 ± 0.33	4.2 ± 0.5
1,2-dichlorobenzene	332 $\mu g\ l^{-1}$	7.63 ± 0.30	6.9 ± 0.4
hexachloroethane	20 $\mu g\ l^{-1}$	8.14 ± 0.35	7.4 ± 1.4

[a] Sorption distribution coefficients ± standard deviation for isotherms determined at 22°C by Curtis (1984).
[b] Mean ± standard deviation of replicated one-point determinations of sorption distribution coefficient, conducted as described in text.

BACKGROUND

Curtis (1984) investigated the sorption characteristics of the bulk sample of aquifer material. He found that sorption of each of the organic solutes over the solution concentration range observed in the field data was well described by a linear isotherm; the intercepts were indistinguishable from zero for all solutes except 1,2-dichlorobenzene. Thus, the sorption isotherms could be adequately represented by the simple expression:

$$q = K_d C \tag{1}$$

where q is the sorbed concentration ($g\,g^{-1}$), C is the aqueous concentration ($g\,m^{-3}$), and K_d is the sorption distribution coefficient ($m^3\,g^{-1}$). The K_d values for sorption at 22°C reported by Curtis (1984) are listed in Table 1.

Using values for the porosity (n) and bulk density (ρ_b) drawn from work at the University of Waterloo (MacFarlane et al., 1983), estimates were made for each of the organic solutes of the expected field retardation factor R (ratio of mean groundwater velocity to mean solute velocity) using the familiar expression (Bear, 1972):

$$R = 1 + \frac{\rho_b}{n} K_d \tag{2}$$

The estimates agreed well with observations of field transport of the organic solutes over relatively short distances (a few m) from the injection zone (Curtis, 1984). Thus, the batch sorption technique as refined by Curtis (1984) appeared to be a very useful method for characterizing local sorption and transport behavior.

It is generally thought that the organic carbon content of soils and sediments controls the sorption of nonpolar organic solutes provided the organic carbon content (f_{oc}) is greater than approximately 0.1% (Schwarzenbach and Westall, 1981; Karickhoff, 1984). The f_{oc} of the bulk sample of Borden aquifer material, however, is only 0.018% (Mackay et al., 1985). In such cases, it has been hypothesized that the mineral surfaces may play a significant role in sorption, especially for the less hydrophobic solutes (Reinhard and Curtis, 1984). In fact, Curtis (1984) found, for the five organic solutes studied, that more sorption was measured than was expected based on the organic carbon partitioning model, which suggests that adsorption onto the mineral surfaces of the bulk sample of Borden sand may have been important.

In the current work, we have modified the sorption technique of Curtis (1984) for investigation of the spatial variability of sorption characteristics in the Borden aquifer. In addition, we have refined and applied techniques for the determination of organic carbon content (f_{oc}) and specific surface area (S_s) of small subsamples of Borden aquifer material, in order to investigate the correlation of these properties with the sorption characteristics.

ANALYTICAL METHODS

Examination of core samples revealed distinct strata, some as thin as 2 cm. Our goal initially was to determine the variability of K_d, f_{oc}, and S_s among the identifiable strata. The consequent constraint was that the total sample mass required by the three analytical methods had to be less than the 60 g or so contained in a 2-cm length of the 5-cm ID core tube. To meet this constraint, we developed or refined methods for measuring K_d and S_s which required much less sample than the methods commonly used. In addition, we applied an organic carbon method which required only small sample masses, after modification to increase its precision.

Sorption

To precisely define a complete sorption isotherm, Curtis (1984) conducted on the order of 10—50 individual batch sorption experiments at varying solution concentration levels; each experiment utilized 45 g of sand, for a total mass requirement of 450—2250 g. Because his results clearly showed that eqn. (1) applied, we recognized that K_d for a given solute and solids sample could potentially be estimated by only one batch sorption experiment conducted at an equilibrium solution concentration within the linear range of the isotherm.

The batch sorption method employed in this work was identical to that of Curtis (1984), except that each experiment was conducted in a 17-ml culture tube with approximately 20 g of aquifer solids, resulting in a solids to liquid ratio of about 2:1 (mass basis). Synthetic groundwater, similar in composition to the native groundwater, was added to the tubes, with precautions to fully saturate the solids and eliminate trapped air. Appropriate volumes of radiolabeled organic solute were injected into the aqueous phase and the tubes were quickly capped, headspace-free, with Teflon-lined septa. The mixture was equilibrated by tumbling at 12 rpm for 72 h, after which the tubes were centrifuged at 2000 rpm for 30 min. A portion of the supernatant was then transferred by syringe and pipetted to a vial for analysis by liquid scintillation techniques. The details of the method, data reduction procedures, and analysis of errors has been discussed by Curtis (1984).

Specific surface area

The specific surface area of solids which do not contain significant quantities of expanding clay minerals, such as the Borden sands (Mackay et al., 1985), is most commonly estimated by a method based on adsorption of nitrogen at liquid nitrogen temperature (77 K). However, we found the nitrogen method required on the order of 10 g of material such as the Borden sands in order to yield accurate and precise results. Consequently, we tested, and subsequently chose to apply, a similar method based on

adsorption of krypton gas at liquid nitrogen temperature, originally proposed for use on low surface area minerals by Beebe et al. (1945). The krypton method was found to be accurate and precise with sample masses of approximately one-half gram. The apparent precision of the method decreased as the heterogeneity of the strata increased, probably due to real differences in the replicate subsamples; for example, the standard deviation for replicate analyses varied from 3—8% for subsamples of relatively uniform strata to approximately 20% for subsamples of heterogeneous strata.

Organic carbon content

A method for organic carbon content determination had been developed in our laboratories for application to sediments such as the Borden sand (M. Reinhard, unpubl. results). The method includes inorganic carbon removal by treatment with phosphoric acid, conversion of organic carbon to carbon dioxide by potassium persulfate digestion in sealed ampules autoclaved for 4 h, and quantification of carbon dioxide with a Dohrmann DC-80 TOC analyzer. Because calcite is known to comprise a large fraction of the Borden sand (~ 10—20%), the inorganic carbon removal step is crucial. A variety of tests were conducted to assess the accuracy and improve the precision of the analysis. The method was found to be accurate to within 15—20% (M. Reinhard, pers. commun., 1984). In replicate analyses, the refined method estimated the organic carbon content of the bulk sample of Borden sand as 0.00018 (0.018%) with a precision of approximately 10%. Similar precisions were observed for replicated analyses of other samples.

Subdivision of the bulk and core samples

Curtis (1984) has described the detailed procedures followed to dry, homogenize, and subdivide the large bulk sample. In brief, the sample was passed through a number 4 sieve and subdivided with a riffle sample splitter into 0.6 and 1.2 kg subsamples. The subsamples were stored in sterilized plastic bags at room temperature in the dark until use.

The core samples discussed herein include one taken in December 1982 (Core Z) and the S-series cores taken in the Fall of 1984. Plan location of the cores is depicted in Fig. 1. Core Z was stored at room temperature for approximately 13 months, at which time it was split vertically and photographed. The core was then logged by an individual familiar with sedimentary petrology in order to delineate the strata. The S-series cores were split and photographed within 1 month of their removal from the field site.

Cores were generally subdivided as follows: All material from one core-half was transferred to a container and homogenized, after air drying. The "homogenized core" sample was stored in the dark at room temperature in a brown glass bottle. The other half was subdivided into specific depth intervals, each of which was homogenized after drying. For Core Z, these

corresponded to the identified strata, which were all inadvertently oven-dried at 130°C. The S-series cores, on the other hand, were subdivided into regular 10-cm intervals and were air dried. For convenience we refer to both types as strata samples. The strata samples were stored in glass bottles until use.

Subsamples for analysis were originally taken from the bulk sample, homogenized Core Z samples, and individual Core Z strata by simple scooping. We found, however, that the precisions of preliminary isotherm determinations as well as other analyses were significantly improved if a small riffle sample splitter was used to prepare subsamples. Consequently, a riffle splitter was used to prepare 20-g subsamples of the S-series core fractions.

RESULTS

Analysis of the bulk sample

In order to calibrate the modified sorption method and determine its precision, complete isotherms and replicated one-point sorption experiments were conducted using the bulk sample of Borden sand. For example, the PCE isotherm derived with the 17-ml culture tubes was found to be linear and statistically indistinguishable from that reported by Curtis (1984). Estimates of K_d were then made for each of the organic solutes (except bromoform) using replicated one-point sorption experiments designed to yield an equilibrium concentration in the range 0.02—0.03 $g\,m^{-3}$ (20—30 $\mu g\,l^{-1}$). The mean and standard deviation of the one-point K_d determinations are listed in Table 1. Although the mean values of the one-point estimates are lower than the K_d's reported by Curtis (1984) by 10—20%, the two estimates are not statistically different. The standard deviation of the replicated one-point estimates ranges from 6 to 19% of the mean value, whereas those for the K_d estimates from the isotherm studies range from 4 to 12%. Thus, as expected, the replicated one-point K_d method is somewhat less precise than the multipoint isotherm method. However, the apparent slight reductions in accuracy and precision are acceptable in light of the relative ease and much reduced mass requirements of the one-point K_d method. Consequently, the one-point method was applied to the analysis of spatial variability of sorption characteristics in the cores.

Analysis of Core Z

Table 2 presents the one-point K_d estimates determined for sorption of each of four of the organic compounds on the different strata of Core Z as well as the homogenized sample of Core Z. For convenience of comparison, the one-point K_d estimates for the bulk Borden sample are also listed in Table 2.

TABLE 2

One-point partition coefficients for Core Z strata, the homogenized sample of Core Z, and the bulk sample

Sample	$K_d \times 10^7$ (g m^{-3})[a]			
	PCE	HCE	1,2-DCB	CTET
Depth intervals (m)				
Core Z strata				
2.320–2.355	6.0	–	–	–
2.355–2.385	8.4	11.2	–	–
2.385–2.460	8.8	12.5	21.3	2.53
2.460–2.620	14.4 ± 1.2[b]	17.4 ± 1.2[b]	35.9 ± 0.8[c]	3.9 ± 0.2[d]
2.620–2.690	16.7	20.7	42.2	3.66
2.690–2.730	11.3	–	–	–
2.730–2.755	–	23.6	–	–
2.755–2.840	8.8	11.3	34.0	2.82
2.840–2.930	6.3	6.5	13.9	1.52
2.930–2.960	7.2	–	–	–
2.960–2.980	4.5	–	–	–
2.980–3.040	6.1	7.5	13.1	1.42
3.040–3.100	8.1	9.4	16.2	3.04
3.100–3.150	7.0	8.0	17.4	–
3.150–3.225	8.5	10.7	21.5	3.26
3.225–3.255	11.6	14.3	–	–
3.255–3.295	10.3	–	–	–
3.295–3.370	6.4	8.0	–	–
weighted average of strata	9.5	12.3	25.6	2.9
Depth-averaged sample				
Core Z	4.3 ± 0.6 (n = 25)	–	–	–
bulk Borden sand	4.2 ± 0.5 (n = 16)	7.4 ± 1.4 (n = 11)	6.9 ± 0.4 (n = 3)	1.3 ± 0.1 (n = 3)

[a] Partition coefficient calculated from single or replicated sorption experiment assuming linear isotherm with zero intercept. For a given compound, initial concentration was the same for all samples, chosen to give equilibrium concentration of approximately 0.030 g m^{-3}. Where no standard deviation (±) is given, only one measurement was made. [b] n = 4 replicates; [c] n = 3 replicates; [d] n = 2 replicates.

Table 2 shows, for sorption of tetrachloroethylene (PCE), that the estimated K_d for the homogenized core sample is statistically indistinguishable from that of the bulk sample. It is also evident that the apparent sorption characteristics vary among the individual strata. However, the mass-weighted averages of the strata K_d's for each compound are significantly higher than the bulk or homogenized core sample values. This discrepancy led to the discovery that the strata had inadvertently been oven-dried overnight after removal from the core. Because the bulk and homogenized core samples had been air-dried at room temperature, it was suspected oven-drying had affected the strata sorptive characteristics. This hypothesis was tested by comparing K_d estimates for sorption of PCE onto two subsamples of sand, one of which had been air-dried and the other of which had been oven-dried overnight. As expected, the oven-drying led to an increase in the measured partition coefficient (by roughly a factor of two).

The mechanism by which overnight oven-drying increases the partitioning of halogenated organic solutes to the Borden sand is not known. In other related work at Stanford University, autoclaving has been observed to increase the partitioning of hexachloroethane onto Borden sand (Criddle, this volume). In addition, Boyd and King (1984) reported similar increases in sorption of 2,3-dichlorophenol and 2,4-dichlorophenol as a result of autoclaving of soil samples. Further investigation of this phenomenon was outside the scope of this effort, but in all subsequent handling and analysis of aquifer solids, special care was taken to air-dry the solids and store them at room temperature under conditions of low and relatively constant humidity.

Because the absolute values of the sorption coefficients for the Core Z strata were increased due to oven-drying, the Core Z data cannot be used to assess the magnitude and scale of variability of the sorption coefficients. Nevertheless, if the strata K_d values are divided by the mass-weighted averages for each compound (where values are available for each compound) and plotted in histogram form as in Fig. 2, a useful observation can be made. In most cases, as Fig. 2 shows, the normalized K_d's for the four compounds are approximately the same for a given stratum. This suggests that a reasonably accurate assessment of spatial variability of sorption properties for a chemically related set of organic compounds (e.g., hydrophobic halogenated organics) can be made by conducting sorption experiments with only one compound. Consequently, in the subsequent work discussed below we conducted replicate sorption analyses with PCE only. PCE was chosen because its sorption coefficient is in the middle of the range of the compounds under investigation and because the field data on PCE distribution in space and time are extensive (Roberts et al., 1985).

Analysis of the S-series cores

As shown in Fig. 1, the plan positions of the S-series cores were along the trajectory of the centers of mass of the migrating solutes. The cores generally

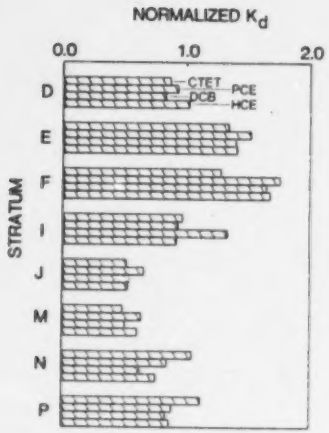

Fig. 2. Normalized distribution coefficients (K_d) for sorption of 4 compounds on 8 strata of Core Z. The strata K_ds were normalized as described in the text. Depth intervals of the strata are listed in Table 2.

sampled the depth interval 2—4 m, a zone traversed by the solutes. The PCE sorption coefficients, organic carbon contents, and specific surface areas of the homogenized samples of five of the S-series cores are presented in Table 3. The results suggest that the average properties of the depth interval sampled do not change significantly along the centerline of the solute movement. The properties of homogenized samples of the seven remaining S-series cores will be determined in the near future to strengthen or modify this conclusion.

At the time of writing, we had completed, for 10-cm depth increments from Core S3, replicate analyses of PCE sorption coefficient and organic carbon content, and single determinations of specific surface area. The results are presented in Fig. 3, in which the strata values are normalized by dividing them by the appropriate homogenized sample value (Table 3). Examination of Fig. 3 reveals that there is significant variability of PCE sorption with depth. The absolute values range over an order of magnitude, with most within a factor of two of the mean. Although there are insufficient data to allow a well-defined estimate of the correlation scale, examination of Fig. 3 suggests that adjacent K_d values are similar over tens of centimeters. This observation, coupled with the fact that the overall variability is significant, suggests that the subdivision of the core into 10-cm intervals may not have obscured detection of important strata of lesser thickness. Furthermore, the vertical variability observed in the sorption coefficients is consistent with estimates of the correlation scale based on grain-size data (O'Hannesin, 1981) and hydraulic conductivity measurements (E. Sudicky, unpubl. results).

Also evident in Fig. 3 is the relative lack of variability with depth in the

TABLE 3

Characteristics of homogenized core samples

Core	K_d for PCE[a] ($m^3\ g^{-1} \times 10^7$)	f_{oc}[b] (%)	Surface area[c] ($m^2\ g^{-1}$)
S1	4.73 ± 0.29	0.015	1.04
S2	4.10 ± 0.21	0.014	1.06
S3	5.56 ± 0.14	0.014	1.04
S8	5.41 ± 0.20	0.014	1.02
S12	4.66 ± 0.21	0.016	0.95

[a] Mean ± standard deviation. [b] Mean values for 1—5 replicates; method error approximately 10%. [c] Mean values for 1—3 replicates; method error less than 10%.

organic carbon content (f_{oc}) and specific surface area (S_s). Figure 3 illustrates that neither the magnitude of the sorption coefficient for a given depth increment nor the variability among increments can be explained by the organic carbon partitioning model. In addition, the observed sorption properties cannot be explained by a two-phase model incorporating both organic carbon content and specific surface area. As a more formal test of the correlation, we conducted a multiple regression analysis of K_d as a linear function of f_{oc} and S_s. Not surprisingly, the correlation was extremely poor ($r^2 = 0.2$). These results indicate, therefore, that the observed sorption properties may be related to the amount and distribution of as yet unidentified mineral phases in the Borden aquifer.

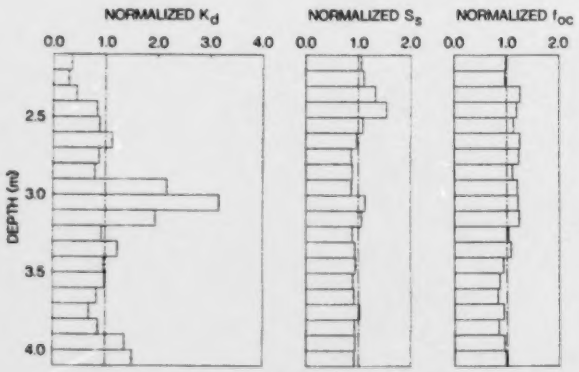

Fig. 3. Vertical variability in Core S3 of: (a) the sorption distribution coefficient (K_d) for tetrachloroethylene (PCE); (b) the specific surface area (S_s); and (c) the organic carbon content (f_{oc}). Normalized values are plotted for 10-cm depth increments.

CONCLUSIONS AND FUTURE WORK

The results of our analyses to date indicate that the average sorption characteristics of the Borden aquifer over the depth interval 2—4 m do not vary appreciably along the centerline of the field transport experiment. Analysis of depth increments in one core has shown, however, that there is significant variation in sorption of tetrachloroethylene (PCE) with depth within the interval 2—4 m; the sorption distribution coefficient for PCE varied over nearly an order of magnitude.

The replicated one-point method of determining the sorption distribution coefficient for an organic solute was found to yield reasonably accurate and precise results with minimal sample mass requirements (60 g for triplicate analyses). Therefore it was possible to investigate sorption variability at a small sampling scale (10-cm depth intervals). Similarly, the methods employed in this study for surface area and solid organic carbon content determination were found to yield accurate and precise results with total mass requirements less than a few grams.

There was preliminary evidence that the sorption distribution coefficients for four halogenated organic solutes, while differing from one another for a given stratum, vary proportionally among different strata. Although additional work is required to confirm the generality of this phenomenon, the preliminary results suggest that, for the Borden aquifer, a reasonably accurate assessment of the spatial variability of sorption distribution coefficients for the organic solutes studied can be obtained from measurements with only one compound.

The results reported herein indicate that the sorption distribution coefficient for PCE is not well correlated with organic carbon content or specific surface area of core strata. Considering the low average organic carbon content of the aquifer solids (0.02%), these results suggest that as yet unidentified mineral phases play a significant role in the sorption of moderately hydrophobic organic solutes.

Studies are underway at Stanford University to elucidate the mineral phases contributing to sorption. We are also continuing our analysis of the S-series cores in order to allow estimation of correlation scales for the sorption characteristics. In addition, by collaborating with the Department of Earth Sciences, University of Waterloo, we are investigating the correlation between hydraulic conductivity and sorption characteristics in the strata of the Borden aquifer.

Our goal in these studies is to amass a detailed understanding of the spatial variability of the properties of the aquifer media that may affect the sorption and transport of the organic solutes. With such a knowledge base, it may be possible to elucidate the dominant phenomena responsible for the variability in solute transport and distribution observed in the field study.

ACKNOWLEDGEMENTS

We thank Ed Sudicky, Bill Blackport, John Bolha, Robert Ingleton, Ray Carter and Stephanie O'Hannesin of the Department of Earth Sciences, University of Waterloo, who each contributed in acquiring, packing, and shipping the core samples. We also thank the following individuals at Stanford University: Claire Tiedeman and Dean Williamson for their careful work in surface area analysis, Gary Hopkins for the organic carbon analysis, and Jimmy Bent for the mineralogical logging of numerous cores. Although the information described in this article has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement CR-808851 to Stanford University, it has not been subjected to the Agency's required peer and administrative review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

Bear, J., 1972. Dynamics of Fluids in Porous Media. Elsevier, New York, N.Y.

Beebe, R.A., Beckwith, J.B. and Honig, J.M., 1945. The determination of small surface areas by krypton adsorption at low temperatures. J. Am. Chem. Soc., 67: 1554–1558.

Boyd, S.A. and King, R., 1984. Adsorption of labile organic compounds by soil. Soil Sci., 137(2): 115–119.

Cherry, J.A., Gillham, R.W., Anderson, E.G. and Johnson, P.E., 1983. Migration of contaminants in groundwater at a landfill: a case study. 2. Groundwater monitoring devices. J. Hydrol., 63: 31–49.

Curtis, G.P., 1984. Sorption of halogenated organic solutes onto aquifer materials: comparisons between laboratory results and field observations. Thesis, Stanford Univ., Stanford, Calif., 113 pp.

Dance, J.T., 1980. Evaluation of reactive solute transport in a shallow unconfined sandy aquifer. M.S. thesis, Univ. of Waterloo, Waterloo, Ont., 93 pp.

Karickhoff, S.W., 1984. Organic pollutant sorption in aquatic systems. J. Hydraul. Eng., 110(6): 707–735.

MacFarlane, D.S., Cherry, J.A., Gillham, R.W. and Sudicky, E.A., 1983. Migration of contaminants in groundwater at a landfill: a case study. 1. Groundwater flow and plume delineation. J. Hydrol., 63: 1–29.

Mackay, D.M., Freyberg, D.L., Roberts, P.V. and Cherry, J.A., 1985. A natural gradient experiment on solute transport in a sand aquifer. I. Approach and overview of results. Water Resour. Res., subm.

O'Hannesin, S.F., 1981. Spatial variability of grain-size parameters and hydraulic conductivity at a dispersion test site. Rep., Univ. of Waterloo, Waterloo, Ont., 46 pp.

Reinhard, M. and Curtis, G.P., 1984. A two-phase model for the sorption of hydrophobic organic solutes by organic matter and inorganic surfaces. Abstracts of the 1984 Int. Chem. Congress of Pacific Basin Societies, Honolulu, Hawaii, Pap. 01F17.

Roberts, P.V., Goltz, M.N. and Mackay, D.M., 1985. A natural gradient experiment on solute transport in a sand aquifer. III. Retardation estimates and mass balances for organic solutes. Water Resour. Res., subm.

Schwarzenbach, R.P. and Westall, J., 1981. Transport of non-polar organic compounds from surface water to groundwater, laboratory sorption studies. Environ. Sci. Technol., 15(11): 1360—1367.

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.